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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT
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INVENTOR(S)/APPLICANT(S)			
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[ ] Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

SELECTIVE GROWTH OF METAL CONTACTS ONTO SEMICONDUCTOR QUANTUM RODS AND TETRAPODS

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ENCLOSED APPLICATION PARTS (check all that apply)

[X] Specification   Number of Pages 14   [X] Applicant claims small entity status. See 37 C.F.R. §1.27

[X] Drawing(s)   Number of Sheets 3 (included   [ ] Other (specify) _____
in the Specification)

METHOD OF PAYMENT (check one)

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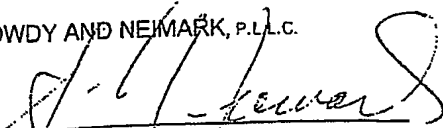[ ] $160 large entity   [X] $80 small entity

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Respectfully submitted,

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Date: February 4, 2004

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Selective Growth of Metal Contacts Onto

Semiconductor Quantum Rods and Tetrapods

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ABSTRACT

Contact of colloidal grown rods, tetrapods and other branched nanostructures to electrode

structures, and their directed assembly into complex circuitry remains a central challenge

for both basic research of electrical transport and for nanodevice fabrication for electrical,

electro-optical and sensing applications. We report a simple method to selectively grow

metal dots on the tips of semiconductor nanorods and tetrapods that can serve as contact

points for wiring them onto complex device architectures. The growth of Au tips onto

CdSe quantum rods and tetrapods is demonstrated and characterized. The size of the Au

tips can be controlled by the concentration of the starting material. Such gold-edge

nanostructures can be self assembled onto electrode structures or to DNA based circuitry.

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Material control on the nanometer scale has witnessed vast and rapid advancements in recent years, expanding the selection of available building blocks for basic studies of scaling laws of material properties on the nanometer scale and for novel device fabrication [1,2,3,4]. Of particular interest are colloidal semiconductor nanocrystals that can be synthesized as rods [5,6], tetrapods [7] and other branched shapes [8], that exhibit promising properties. For example, semiconductor quantum rods have already been demonstrated to have considerable advantages over dots for several applications including improved performance in photovoltaic cells on account of better charge transport properties [9], and enhanced optical gain as compared to spherical dots while providing polarized lasing [10]. To realize fully the potential of miniaturization with such colloidal prepared nano-building blocks, a primary challenge lies in finding an effective wiring scheme, based on the powerful principles of self-assembly, to connect these to electrodes and hence to the 'outside' world. The problem of contact reproducibility and contact resistance has hindered the ability to fully understand conductance in nanotubes and nanowires, and only recently there have been encouraging reports for good connectivity for such micron-long one-dimensional structures [11,12,13]. However, wiring of significantly shorter semiconductor rods and other branched architectures, with arm lengths of less then 100 nm, is a long standing open issue. The use of bifunctional organic ligands, primarily dithiols, as contacting ligands that has been employed for STM studies [14] and also in source-drain transport measurements [15], creates a tunneling barrier and often transport is dominated by the contact resistances. The employment of DNA based assembly for creating functional circuitry [16, 17] also requires selective anchor points for the directed assembly of nanostructures [18]. Here we report a new and simple method to grow selectively gold dots

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onto the tips of nanorods and tertrapods, resulting in formation of a natural point of contact to wire these nanoobjects onto electrode structures, and a natural anchor point for further directed self assembly.

Our method for selective growth of contacts entails dissolving $AuCl_3$ in toluene by use of dodecyldimethylamonium bromide (DDAB) and dodecylamine, and mixing this solution with a toluene solution of colloidal grown nanorods or tetrapods. No reduction agent is purposefully added. The method is exemplified here for the prototypical CdSe nanocrystal system that is highly developed synthetically and widely studied for its size and shape dependent properties [5,19], and is obviously applicable to other semiconductor nanocrystals. CdSe rods and tetrapods of different dimensions (see below), were prepared as described elsewhere, by high temperature pyrolisys of suitable precursors, in a coordinating solvent containing a mixture of trioctylphosphineoxide (TOPO), and of phosphonic acids [5,8,20]. In a typical experiment a gold solution was prepared containing 12 mg $AuCl_3$ (0.04mmol), 40 mg of DDAB (0.08mmol) and 70 mg (0.37mmol) of dodecylamine in 3 ml of toluene and sonnicated for 5 minutes. The solution changed color from dark orange to light yellow. 20 mg of CdSe quantum rods of the required dimensions were dissolved in toluene in a three neck flask. The gold solution was added drop-wise over a period of three minutes. During the addition, the color gradually changed to dark brown. Following the reaction, the QR's were percipetated by addition of methanol and separated by centrifugation. The purified product could then be easily redissolved in toluene for further studies.

Figure 1 presents transmission electron microscopy (TEM) images clearly showing the effect of Au growth onto CdSe quantum rods of dimensions 30x4 nm (length x diameter).

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Frame A shows the rods before Au growth, while in frames B-D, the gold growth procedure was performed as described above adding gradually larger amounts of Au precursors (see Fig. 1 caption for details). In frames B-D, selective Au growth onto the rod edges is clearly identified as the appearance of points with enhanced contrast afforded by the higher atomic number of the Au compared with CdSe. The rods now appear as 'nano-dumbbells'. More over, by controlling the amount of initial Au precursor, it is possible to control the size of the Au tips on the nano-dumbbell edges, from ~2.3 nm in Fig. 1B, to ~3.3 nm in Fig. 1C, to ~4.2 nm in Fig. 1D. The procedure clearly leads to the growth of natural contact points on the edges of the rods.

To verify the material content and structure of the gold on the rod tips we employed several structural and chemical characterization methods as can be seen in Fig. 2. Figure 2a shows the powder Xray-diffraction pattern for the 30x4 nm rod sample comparing the rods before (bottom) and after (top) gold growth. The appearance of the Au (111), (200) and (220) peaks is evident following Au growth. EDS analysis of a micron area of rods after growth is shown in Figure 2b, and the appearance of Au in the goldenized and purified rod sample is also clear from the appearance of the Au peak.

Further evidence for Au growth onto single rods, is provided by HRTEM (high resolution TEM) studies of the nano-dumbbells. Figure 2C shows a HRTEM image of a single rod after gold treatment. The lattice image for the rod part composed of CdSe is seen to correspond to growth of rods along the CdSe (001) axis, consistent with the earlier studies for rod growth [5,7,20]. The Au is discerned once again as the region at the edge with enhanced contrast. It is difficult, because of the significant different contrast of the CdSe versus Au, to discern clearly both lattice images simultaneously, but in different

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imaging conditions we could verify the presence of the CdSe lattice in the center as seen in figure 2C, and the Au lattice in the edges.

The method for selective Au growth could be easily expanded and applied to rods of arbitrary dimensions, and to tetrapods. Figure 3 shows TEM images for three rod samples of dimensions 12x4 nm (Fig. 3A, B), 30x4 nm (Fig. 3C, D), and 60x6 nm (Fig. 3E, F), before and after Au treatment. The presence of the high-contrast tips on the treated rods, forming nano-dumbbells, is evident in all cases. Highly selective edge growth is discerned and demonstrated for three rod sizes and could easily be applied to arbitrary rod sizes. The distribution quality of the longer rod sample is not as homogeneous as the shorter ones, yet Au growth on edges is resolved clearly also here. In addition the method was applied to a CdSe tetrapod sample, as can be seen in Fig. 2G, H showing several tetrapods (Fig. 2G), and an enlargement of one tetrapod (Fig. 2H), after performing the Au growth process. In this case, the growth occurs selectively on all the edges of the tetrapods leading a tetrahedral arrangement for the Au tips, and once again providing the natural contact points for this unique structure.

The reaction mechanism for the gold growth should entail a reduction of Au from its 3+ oxidation state in $AuCl_3$ to the 0 oxidation state in the metal. This requires availability of electrons but no obvious reduction agent has been added in our procedure. Surfactant agents can complex with Au and change its oxidation state to +1 [21], but still the formation of the Au metal in the 0 oxidation state requires reduction. The electrons are supplied for the reaction by two alternative mechanism – either a photoreduction, through absorption of light in the rod forming an electron-hole pair where the electron can be

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available for Au reduction, or by the irradiation with an electron beam (for example in the TEM), which can supply the necessary electrons.

The specificity of edge growth can thus be related to the preferential adsorption of the Au complex onto the rod edges. The edges are more reactive due to the imperfect passivation of the ligands on these faces. Once Au nucleates on the edge, it is preferential for additional Au to adhere and grow on that existing seed. This gains support from controlling the extent of Au growth on the rod edges by using increased concentration of Au in the gold solution as was shown in figure 1. Moreover, careful examination of early Au growth as shown in Fig. 1B reveals that in some rods preferential early growth occurs on one edge. This conforms with the surfactant-controlled growth model suggested for CdSe rods [5,7,20]. In this mechanism, one of the rod edges is Cd rich and hence relatively well capped by the phosphonic acids while the opposite rod edge is Se rich and hence more labile for further reaction and in this case for adhesion of the Au complex which readily yields Au metal growth as demonstrated above. From the viewpoint of chemical reactivity, the asymmetry in reaction to selectively occur at the edges versus the rest of the structure is fascinating.

We also note that in some cases we can identify Au growth on branching and defect points, but at slower rate compared to the distinctive edge growth discussed above. This can be seen in Fig. 2E and 2G, where weak dark Au spots appear also in some positions other then the edge of the long rods and tetrapods. This growth can be controlled by the amounts of Au added to the rods and conforms with the above picture in that at such points there is increased reactivity due to the imperfect chemical bonding. Those serve as advantageous adsorption sites for the Au complex. We emphasize that the edge growth

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occurs more readily then growth on the defects and hence can be controlled to achieve contact points.

It is important to note that the method could easily be expanded to additional semiconductor nanocrystal systems and to additional metals, to tailor the metal edge contact as desired.

With such fine control of this procedure for growing natural metal contacts onto the tips of rod and branched semiconductor particles we next discuss the unique properties of these nano-heterostructured systems. The first obvious application for the Au tips is in serving as electrical contact points. Several strategies can be employed to realize such contacts. It is possible to deposit the metallized nanorods or the other branched structures onto a substrate, identify their position, and then write by electron-beam lithography electrodes to overlap with the Au tips, as was previously performed with nanotubes and nanowires [11,12,13]. In a different strategy, it is also possible to deposit the goldenized rods onto pre-existing electrode structures, with or without electrostatic trapping by an applied electric field [22]. Additionally, for such chemically processable nanorods and branched structures it is possible to apply the powerful approaches of self assembly, using for example, DNA templates for creating the connections as was recently demonstrated for carbon nanotubes creating a transistor [18].

Aside from serving as natural contact points, such Au, or more generally metal edges, can also impart the rods with advantageous and novel properties in several other directions. First, we expect enhanced linear and non-linear optical properties in such a system. The polarizibility of such a structure may obviously be significantly increased compared with that of the regular rods. We foresee possibilities for enhancement in second harmonic

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generation [23] and also the observation of novel plasmon resonances related to highly controlled distances that could be tailored for the Au particles at the edges of rods [24,25].

Such Au or metal tipped rods and tetrapods offer new objects for directed self assembly where the edges can serve as selective anchor points for ligands and chemistries preferential for the Au surface. They may also be envisioned as selective growth points for additional materials via a seeded growth solution-liquid-solid mechanism as was recently demonstrated in growth of III-V semiconductor quantum rods [6].

New nano-dumbbells and metalized nanostructures offer possibilities for realizing novel electrical, optical and sensorial nano-devices.

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FIGURE CAPTIONS:

Figure 1: Controlled growth of Au onto the tips of CdSe quantum rods. TEM images are shown for A. Original 30x4 nm rod sample. B. Rod sample after Au treatment using 10 mg of rods, 4 mg $AuCl_3$, 25 mg DDAB and 40 mg dodecylamine. C. Rod sample after Au treatment using 10 mg of rods, 8 mg $AuCl_3$, 50 mg DDAB and 90 mg dodecylamine. D. Rod sample after Au treatment using 10 mg of rods, 13.5 mg $AuCl_3$, 100 mg DDAB and 160 mg dodecylamine.

Figure 2: Structural and chemical characterization of CdSe-Au 'nano-dumbbells'. A. Powder Xray diffraction comparing CdSe rods before (bottom), and after (top) Au growth. CdSe and Au peaks are marked. Au clearly appears after the growth process. The unusual intensity of the (002) CdSe peak in the original rods is a result of partial alignment in the deposited rod sample. B. Energy dispersive Xray spectroscopy (EDS) spectrum on the goldenized CdSe rod sample. The relative percentage of Au:Cd:Se was 41.6%:40%:18.4% C. HRTEM image of a single nano-dumbbell. The CdSe lattice for the rod in the center, and Au tips at the rod edges, can be identified.

Figure 3: Au growth on tips of various CdSe quantum rods and CdSe tetrapods. A, B. 12x4 nm quantum rods before and after Au growth, respectively. C, D. 30x4 nm quantum rods before and after Au growth, respectively. E, F. 60x6 nm quantum rods before and after Au growth, respectively. G, H. Au growth on CdSe tetrapods showing a general view (G), and higher magnification image for one tetrapod (H).
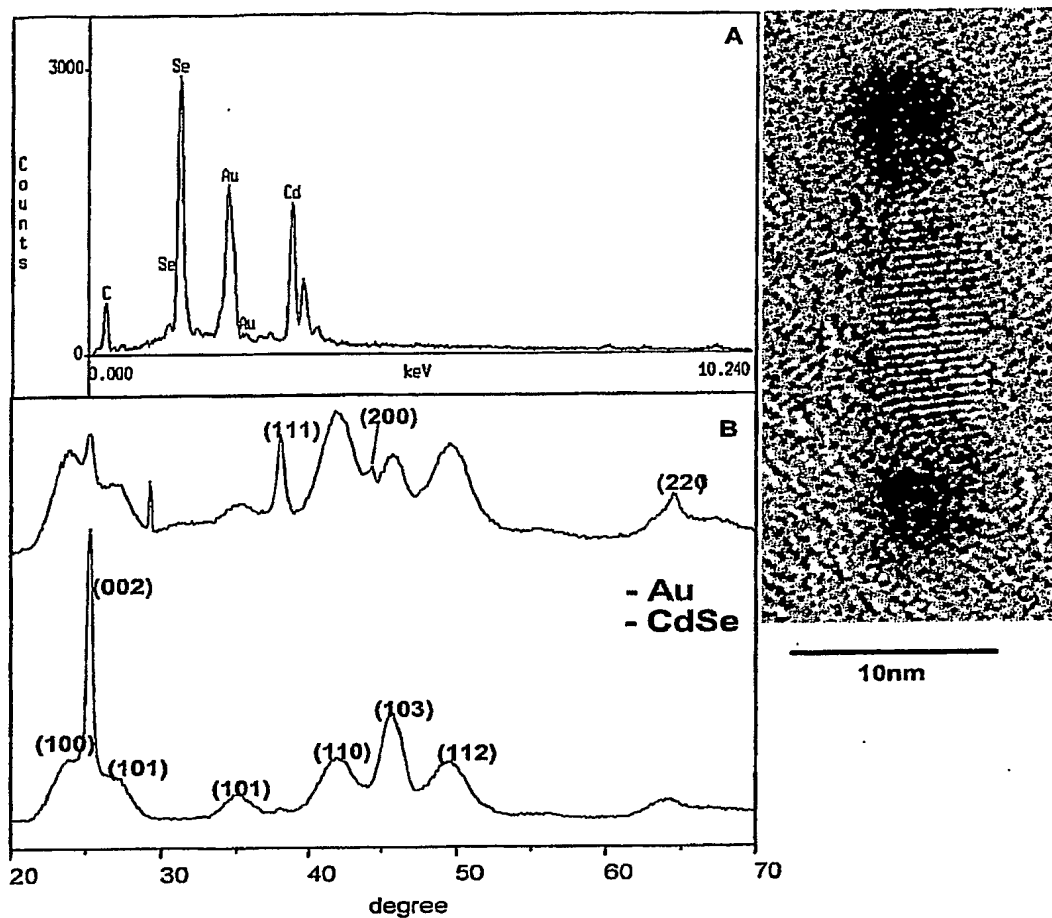
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Figure 1

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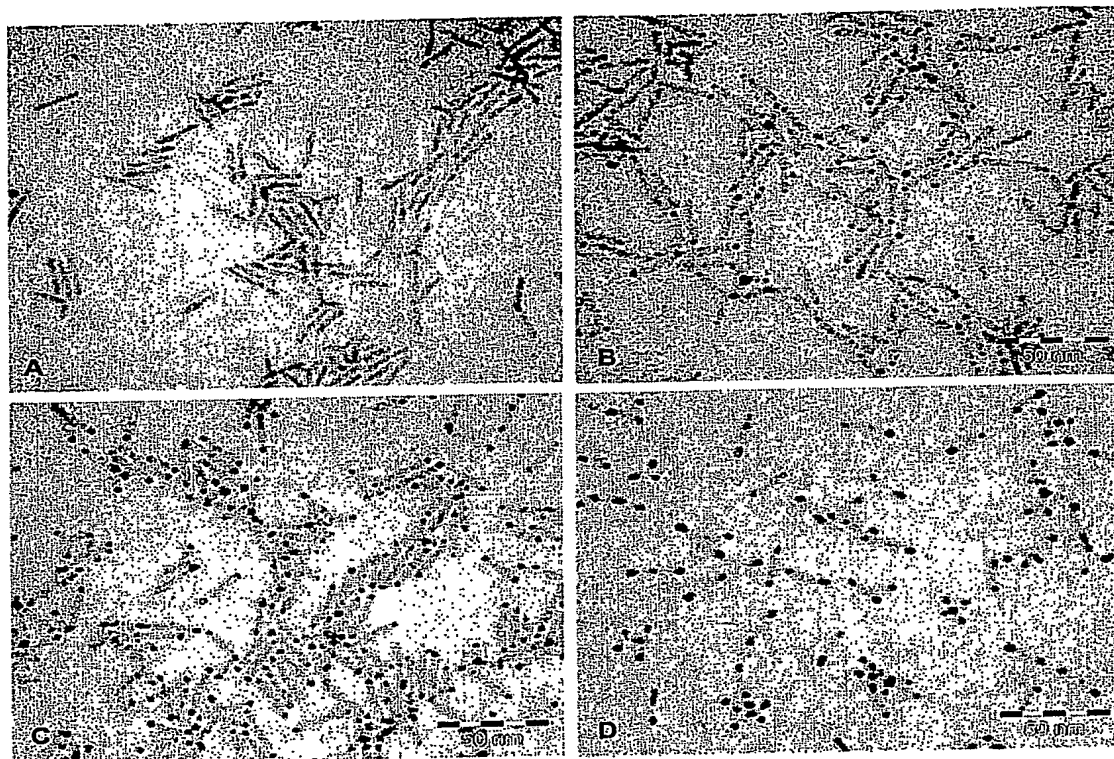
Figure 2

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Figure 3

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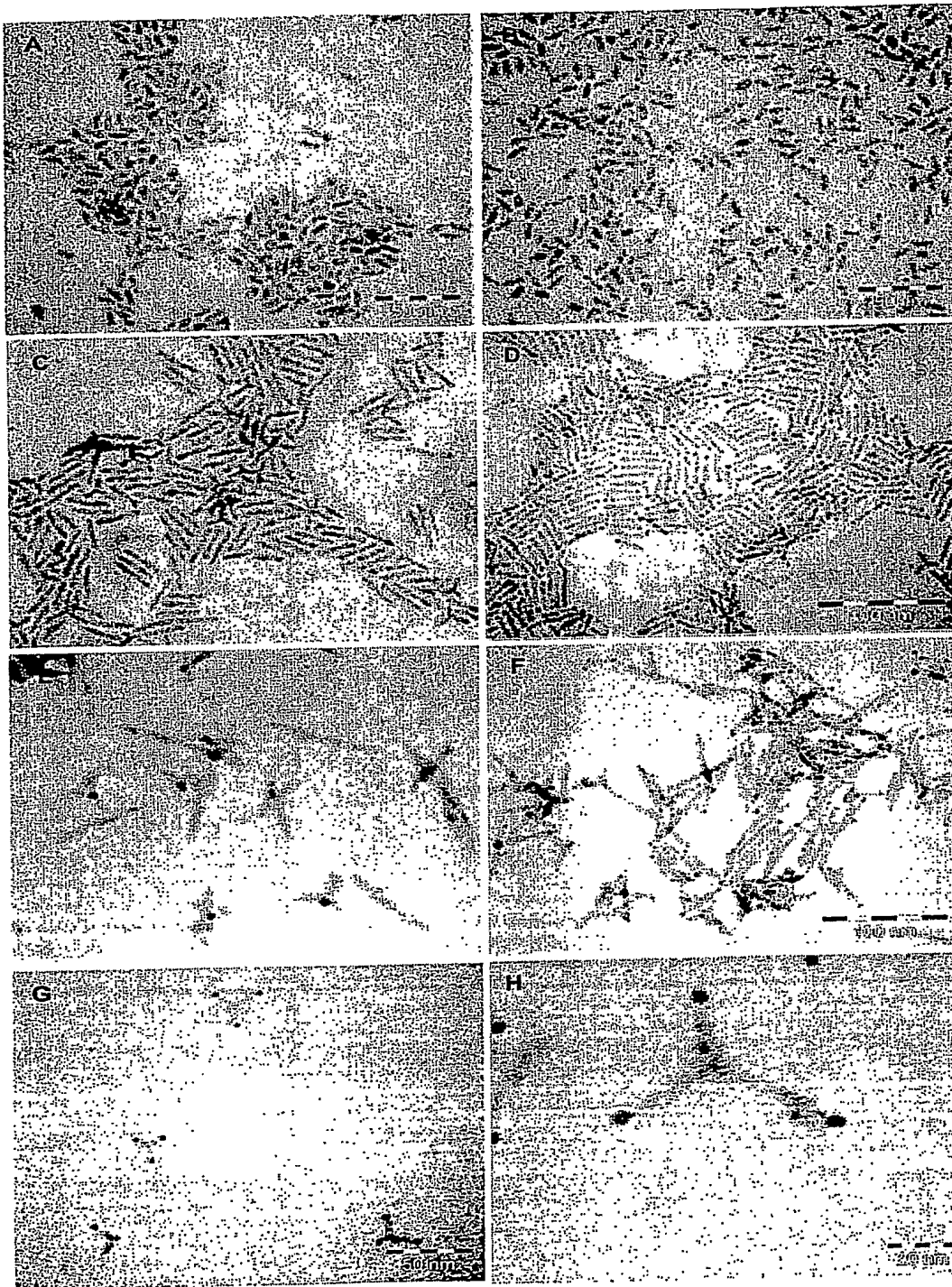**REERENCES:**

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